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Hoppema, M; Fahrbach, E; de Baar, H.J.W.

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# Surface layer balance of the southern Antarctic Circumpolar Current (prime meridian) used to derive carbon and silicate consumptions and annual air-sea exchange for CO<sub>2</sub> and oxygen

Mario Hoppema

Department of Tracer Oceanography, University of Bremen, Bremen, Germany

Eberhard Fahrback

Alfred-Wegener-Institut für Polar- und Meeresforschung, Bremerhaven, Germany

Hein J.W. de Baar

Netherlands Institute for Sea Research, Texel, Netherlands

**Abstract.** A simple model, using concentrations of nitrate and phosphate in austral winter 1992, reveals that the Antarctic Surface Water (AASW) of the southernmost Antarctic Circumpolar Current (ACC) between the Southern ACC Front and the Weddell Front is made up of ~90% Upper Circumpolar Deep Water (UCDW) and 10% northward flowing AASW from the Weddell Gyre. With a typical timescale of ~1 year the upwelling velocity was calculated to be as high as 60–100 m yr<sup>-1</sup>. Knowing the composition of the surface water with respect to its sources, changes due to several processes in the surface layer were deduced for carbon dioxide, oxygen, and silicate. As the timescale of changes in the surface layer of the southern ACC is ~1 year, this allows us to calculate changes on an annual basis without interference of short-term variations. Balancing the contributions by upwelling, biological activity, and air-sea exchange to the concentrations in the surface layer, the area was found to be a large sink for atmospheric oxygen of 6.0 mol m<sup>-2</sup> yr<sup>-1</sup> (53 μmol kg<sup>-1</sup>) and a small sink for atmospheric carbon dioxide of 1.0 mol m<sup>-2</sup> yr<sup>-1</sup> (9 μmol kg<sup>-1</sup>). The most important cause for the oxygen sink is the upwelling of oxygen-poor UCDW, which surpasses the oxygen-elevating effect of primary productivity. This large oxygen sink, in between areas to the north and south which are only a small sink or even a source, conforms with the latitudinal distribution of atmospheric oxygen. The small CO<sub>2</sub> sink is largely brought about by biological activity. The annual carbon utilization amounts to 76 ± 22 g C m<sup>-2</sup> yr<sup>-1</sup>, which is relatively high for an open ocean region in the Antarctic. However, it supports recent estimates of primary production of the Antarctic Ocean that are higher than early published values. The annual silicate consumption was calculated to be 126 ± 19 g Si m<sup>-2</sup> yr<sup>-1</sup>. This is considerably higher than the Southern Ocean mean in current estimates. Although the southernmost ACC may be atypical for the Southern Ocean, the current estimate for Southern Ocean silica production may well be an underestimation. The silicate to carbon utilization ratio derived here is 0.53 which aligns with investigations on Antarctic phytoplankton and thus underscores the consistency of our results.

## 1. Introduction

The Antarctic Circumpolar Current (ACC) is the largest coherent current structure in the world ocean. It connects all major oceans and acts as the prime water distributor for the ocean basins. The principal water mass of the ACC is the Circumpolar Deep Water (CDW) which originates from the deep water masses of these ocean basins. The CDW ascends poleward over the northward flowing dense Antarctic Bottom

Water produced in areas close to the Antarctic continent. The CDW consists of two cores, the Lower Circumpolar Deep Water (LCDW) deriving essentially from the North Atlantic Deep Water, which joins the ACC in the Atlantic sector, and the shallower Upper Circumpolar Deep Water (UCDW), which is part of the mainstream continuing its circumpolar path from the Pacific sector. The main flowing direction of the ACC is eastward, and the water transport occurs predominantly in a few major current bands which largely coincide with the positions of the frontal systems of the ACC [Whitworth and Nowlin, 1987; Orsi *et al.*, 1995].

By virtue of its physical properties, the ACC represents one of the most remarkable features of the world ocean. The seafloor underneath the ACC is the most important area

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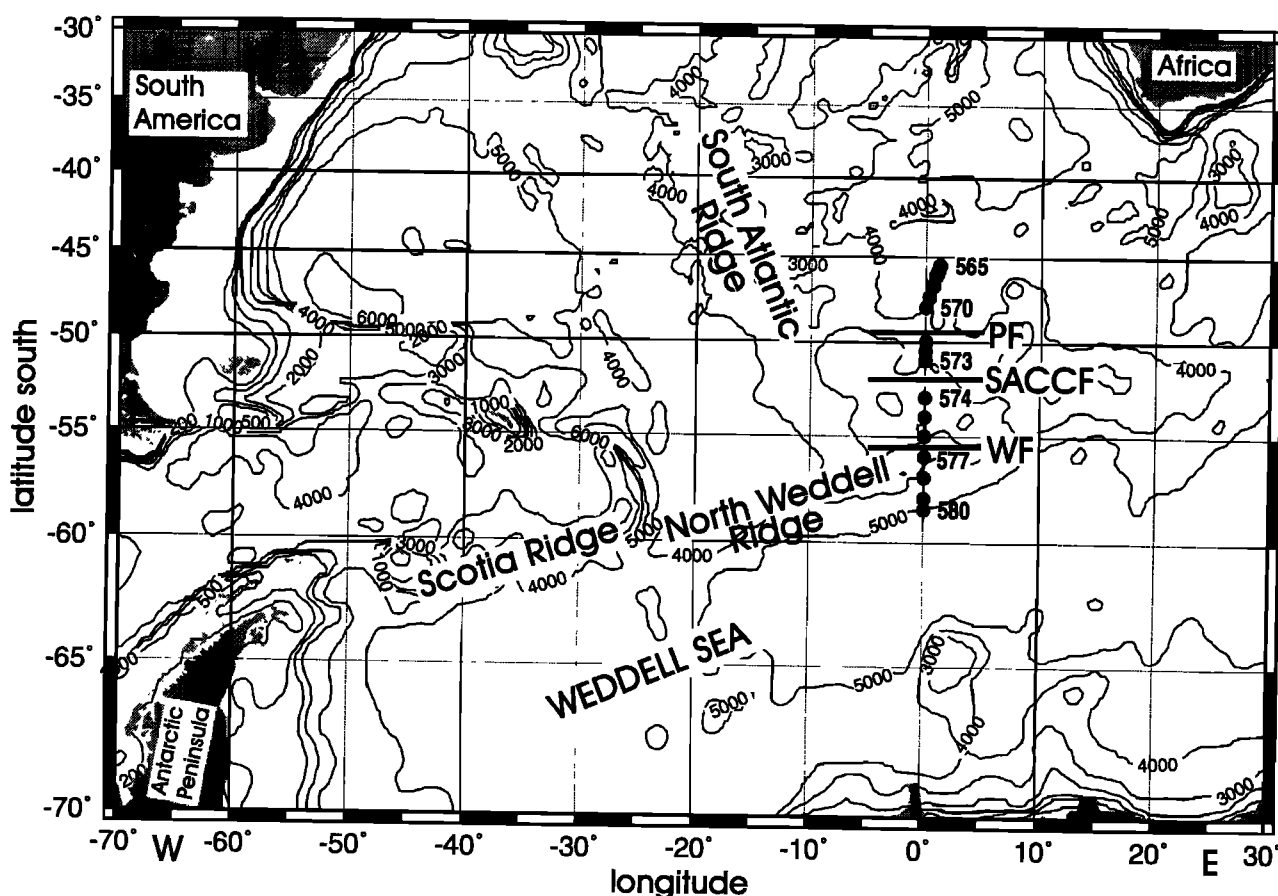
where biogenic silica (opal) accumulation occurs [DeMaster, 1981]. Most of the ACC is thought to be less productive [Jacques, 1989; Banse, 1996], although it is persistently repleted in major nutrients. This renders the ACC one of the most prominent High Nutrient Low Chlorophyll (HNLC) regions. Estimates of the total production of organic matter in the Antarctic are accordingly low, which would imply a rather low drawdown of carbon dioxide by phytoplankton production in this region. On the other hand, the frontal systems, especially the Polar Front [Lutjeharms *et al.*, 1985; De Baar *et al.*, 1995] and also the southern boundary [Tynan, 1998], have been identified as areas of enhanced phytoplankton productivity.

Many investigations have emphasized the highly variable characteristics of the carbon dioxide distribution in the surface layer of the ACC [e.g., Poisson *et al.*, 1993; Bellerby *et al.*, 1995; Bakker *et al.*, 1997]. The difference in  $\text{CO}_2$  partial pressure ( $\text{pCO}_2$ ) between the atmosphere and the surface ocean, which governs the air-sea exchange, is dependent on many physical and biological factors such as sea surface temperature, wind action, and phytoplankton growth. A variable physical and biological environment in the ACC causes a large variability of surface water  $\text{CO}_2$ . As long as the extent and rates of these processes and the factors that

influence them are not sufficiently known, it will be impossible to satisfactorily assess the air-sea flux of  $\text{CO}_2$  on an annual basis from the few  $\text{pCO}_2$  measurements. In this study we apply a different, indirect approach for obtaining the  $\text{CO}_2$  flux between the ocean and the atmosphere. All possible  $\text{CO}_2$  changes in the surface layer of the southern ACC were balanced to give the annual fluxes of the  $\text{CO}_2$  air-sea exchange. Previously, this method has been applied to the Weddell Sea [Hoppema *et al.*, 1999]. This approach also yields an estimate of the annual carbon utilization (primary productivity). We also apply the concept to oxygen and silicate data, which yields estimates of the annual air-sea flux of oxygen and the annual silicate utilization.

## 2. Sampling and Methods

Data presented are from cruise ANT X/4 of the German research vessel *FS Polarstern* during early austral winter in June 1992 [Lemke, 1994]. All stations in the present study are situated near or on the prime meridian between Africa and Antarctica ( $0^\circ$  longitude; Figure 1). Water for the determination of oxygen, total  $\text{CO}_2$ , silicate, nitrate, and phosphate was taken from a rosette system with 24 Niskin samplers (12 L) coupled to a conductivity-temperature-depth (CTD)



**Figure 1.** Map of the South Atlantic Ocean, including the Atlantic sector of the Southern Ocean with the position of the stations. Approximate locations of the hydrographic fronts are indicated. The Southern Ocean is defined as the region south of the Subtropical Front (at  $\sim 40^\circ\text{S}$  on the prime meridian). PF, Polar Front; SACC, Southern Antarctic Circumpolar Current Front; WF, Weddell Front.

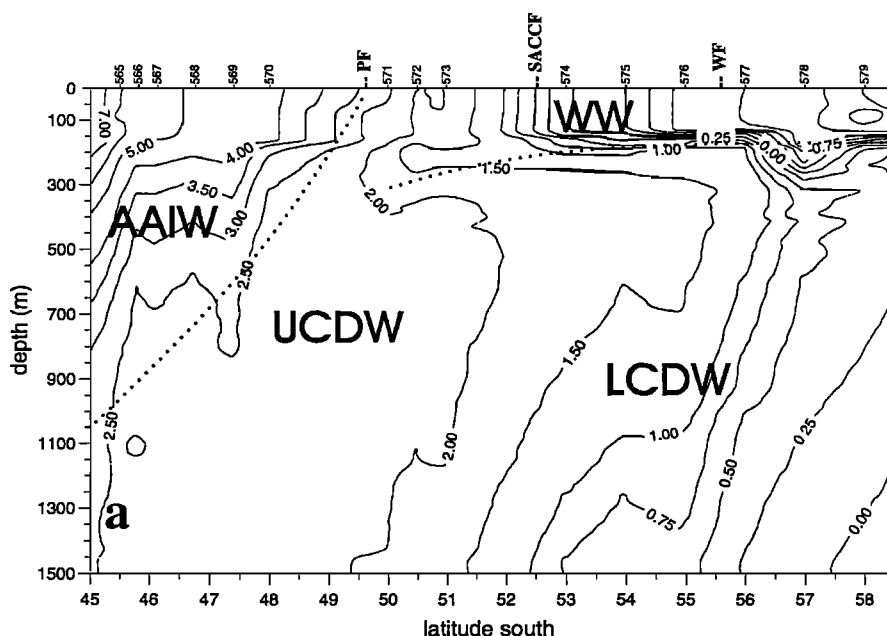
sensor. Total CO<sub>2</sub> (TCO<sub>2</sub>), the sum of all inorganic carbonate species dissolved in seawater, was analyzed with a standard coulometric technique [Johnson *et al.*, 1987]. Saturated mercury (II)-chloride was added (0.5 mL on a sample bottle of 500 mL) as a preservative to samples from the upper 250 m. All analyses were performed within 24 hours, but most within 12 hours of sampling. Prior to analysis, samples were stored in the dark at lab temperature. The mean difference of 83 duplicates was 0.9  $\mu\text{mol kg}^{-1}$ . Unfortunately, on this cruise we did not have available the now widely used certified reference material of A. Dickson of the Scripps Institution of Oceanography (La Jolla, California). On another cruise in the same region some months later (leg ANT X/7), where the same equipment was used, this certified reference material was used for setting the accuracy. The ANT X/4 data set was then standardized, using accurate data of cruise ANT X/7 in the following way: TCO<sub>2</sub> was plotted versus potential temperature  $\theta$  for all offshore Weddell Sea stations, and regression lines were calculated for the temperature range -0.6 to -0.1°C. This range falls within the Weddell Sea Deep Water, TCO<sub>2</sub> values of which are deemed to be seasonally invariable. The ANT X/4 data were corrected such that the  $\theta$ /TCO<sub>2</sub> relationship was consistent with the ANT X/7 data. This procedure was justified by comparing the  $\theta$ /oxygen relationships of both cruises.

Dissolved oxygen was determined on board on discrete samples using a standard automated Winkler technique with photometric end point detection, precision 0.2%. Concentrations of silicate, nitrate, and phosphate were determined colorimetrically using a Technicon Autoanalyzer-II-System as described by Kattner and Becker [1991].

Samples were generally analyzed immediately after sampling. In a few cases the samples were stored 4°C in the dark, but never for longer than 6 hours. All measurements were done in duplicate; precision was estimated at 0.3  $\mu\text{mol kg}^{-1}$  for silicate, 0.1  $\mu\text{mol kg}^{-1}$  for nitrate, and 0.01  $\mu\text{mol kg}^{-1}$  for phosphate. The accuracy was established by running four standards at the beginning and two standards at the end of each run.

### 3. Results

In Figure 2 vertical sections of the prime meridian extending to 1500 m depth are shown for a suite of parameters. To the north, this section is bordered by the Subantarctic Front. The section crosses the Polar Front, the Southern ACC Front, and the Weddell Front (ACC-Weddell boundary) as described by Orsi *et al.* [1995]. All water of this section flows eastward as part of the ACC (see Spiridonov *et al.* [1996], in which some hydrographic data of cruise ANT X/4 are shown). The surface layer consists of Antarctic Surface Water. It has relatively low concentrations of TCO<sub>2</sub> and nutrients and high concentration of oxygen. The properties of the Antarctic Surface Water (AASW) along this transect have a wide range of characteristics, with clear gradients between the northern part (ACC) and the southern part (Weddell Sea) for all parameters (Figure 2). Northward of the Polar Front (PF), the isolines that describe the surface water of the south bend downward. This illustrates the formation of Antarctic Intermediate Water (AAIW). At the northern end of our section (Figures 2c and 2g) the oxygen maximum, which together with the salinity minimum is a



**Figure 2.** Vertical sections for the upper 1500 m of the water column contoured for (a) potential temperature (°C), (b) potential density anomaly ( $\sigma_0$ ), (c) salinity, (d) nitrate ( $\mu\text{mol kg}^{-1}$ ), (e) phosphate ( $\mu\text{mol kg}^{-1}$ ), (f) total CO<sub>2</sub> ( $\mu\text{mol kg}^{-1}$ ), (g) dissolved oxygen ( $\mu\text{mol kg}^{-1}$ ), (h) silicate ( $\mu\text{mol kg}^{-1}$ ) across the Antarctic Circumpolar Current along the prime meridian between 45°S and the northern Weddell Sea. TCO<sub>2</sub> data of this section are also given by Hoppema *et al.* [2000]. In the potential temperature section (Figure 2a) the approximate water mass boundaries are indicated, where WW is Winter Water (Antarctic Surface Water), AAIW is Antarctic Intermediate Water, UCDW is Upper Circumpolar Deep Water and LCDW is Lower Circumpolar Deep Water. PF, Polar Front; SACCF, Southern ACC Front; WF, Weddell Front.

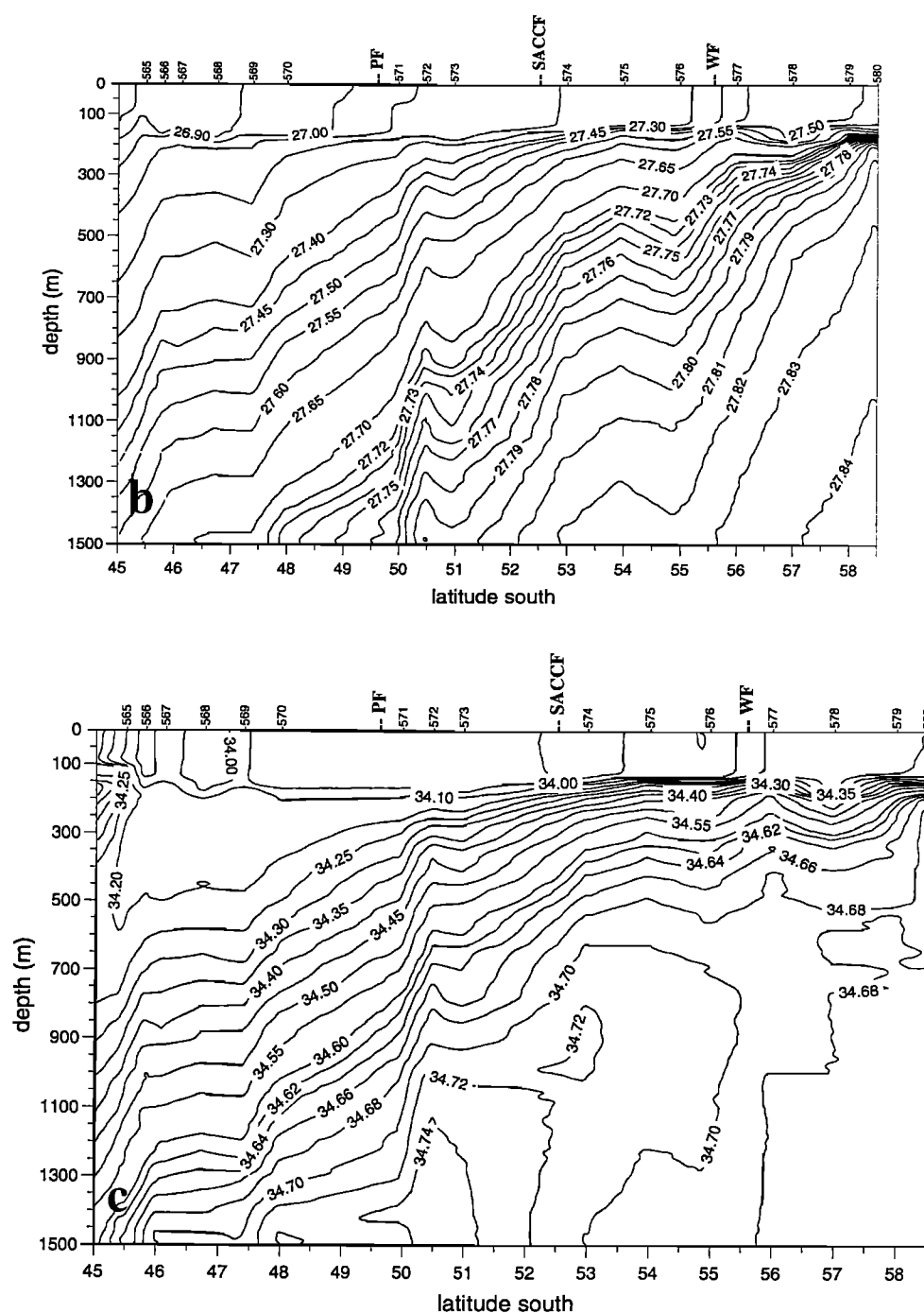


Figure 2. (continued)

hallmark of this northward spreading water mass, can be seen.

Underneath the AAIW between 45° and 49°S,  $\text{TCO}_2$  and nutrient maxima and an oxygen minimum can be discerned (Figures 2d-2g). Toward the south, these maxima ascend, e.g., from 1500 m depth at 46°S to 400 m at 54°S (Figure 2). These extrema are characteristic of the Upper Circumpolar Deep Water (UCDW). Between 51° and 55°S a temperature maximum is also found in this UCDW core (Figure 2a). Underneath the UCDW, maxima of  $\text{TCO}_2$ , nutrients, and salinity are observed (Figures 2c-2f). These describe the core of LCDW, a relatively young core of CDW which derives predominantly from the North Atlantic Deep Water. In the Weddell Sea (south of the Weddell Front), UCDW is not

found anymore [Orsi *et al.*, 1995], implying that UCDW is entrained into the surface layer of the southern ACC. In the ACC the concentrations of  $\text{TCO}_2$ , nutrients, and oxygen in the abyss show an increase toward the bottom. This is due to the Antarctic Bottom Water, which spreads northward over the seafloor.

## 4. Balance Calculations

### 4.1. Composition of the Surface Layer of the Southernmost ACC

In the southernmost area of the ACC, that is, the area north of the Weddell Front, the water of the surface mixed layer

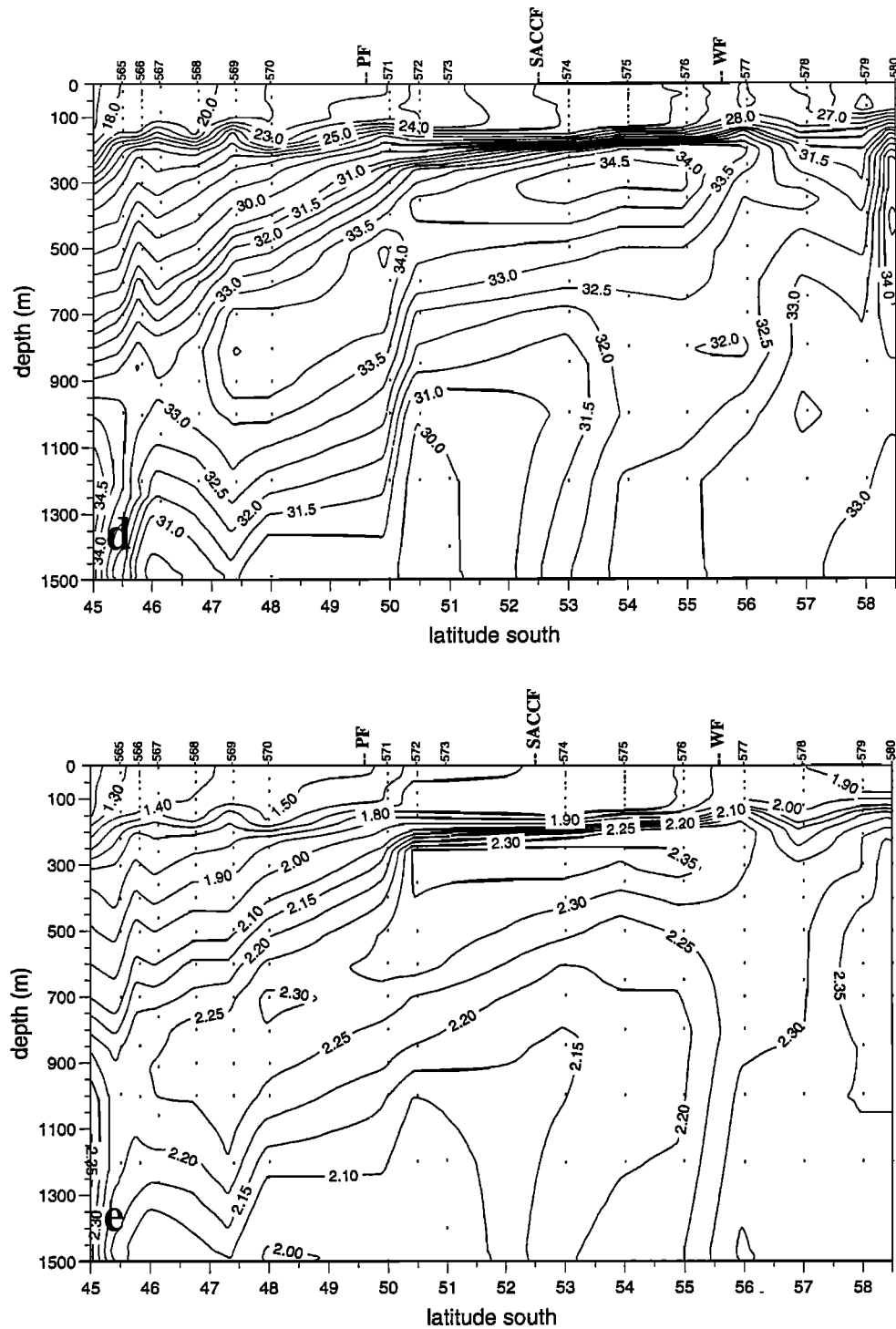


Figure 2. (continued)

(AASW) is formed from two sources, as shown in a schematic representation in Figure 3. The first is the AASW of the Weddell Sea, which is transported northward by Ekman transport due to the divergent nature of the Weddell Gyre [De Szoeke and Levine, 1981]. The second is upwelled water from subsurface layers, notably the UCDW. We calculate the fractions of both sources for the AASW of the southern ACC. As surface water is concerned, temperature, salinity and the dissolved gases  $\text{CO}_2$  and  $\text{O}_2$  are not suitable for such a calculation because they are nonconservative.

Nitrate and phosphate are also nonconservative in the surface layer owing to biological activity, but, using these two nutrients and a constant Redfield ratio, the relative contributions of UCDW and AASW of the Weddell Sea surface water to the AASW of the southernmost ACC can be calculated as follows (see also Figure 3):

$$F_{\text{UCDW}} * [\text{UCDW}(\text{NO}_3)] + (1 - F_{\text{UCDW}}) * [\text{WS}(\text{NO}_3)] \\ = [\text{ACC}(\text{NO}_3)] - \Delta(\text{NO}_3)_{\text{bio}} \quad (1)$$

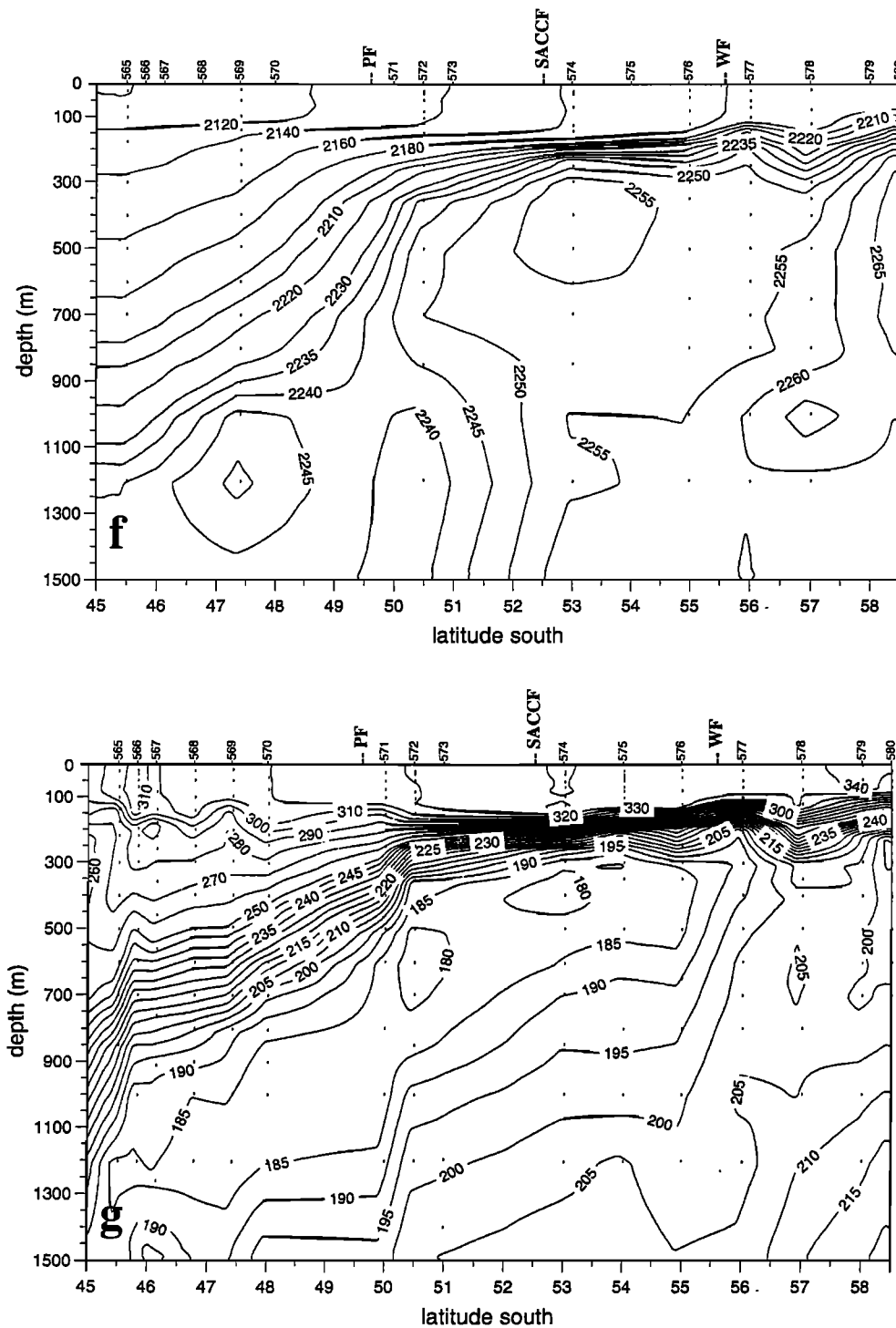


Figure 2. (continued)

$$FUCDW * [UCDW(PO_4)] + (1 - FUCDW) * [WS(PO_4)]$$

$$= [ACC(PO_4)] - \Delta(PO_4)_{bio} \quad (2)$$

$$\Delta(NO_3)_{bio} / \Delta(PO_4)_{bio} = 15.1, \quad (3)$$

where  $FUCDW$  is the fraction of UCDW;  $[UCDW]$ ,  $[WS]$ , and  $[ACC]$  are the concentrations in the UCDW, the AASW of the Weddell Sea, and AASW of the southernmost ACC, respectively, and the actual property is within parentheses.

$\Delta(NO_3)_{bio}$  and  $\Delta(PO_4)_{bio}$  are the changes in nitrate and phosphate caused by biological activity. The value of 15.1 in equation (3) was obtained by plotting the surface and subsurface data in the area north of the Weddell Front (Figure 4a). The concentrations of the different end-members used in this calculation appear in Table 1 together with those of  $TCO_2$ , oxygen, silicate, salinity, and temperature. The concentrations in Table 1 are from areas ~250 km on either side of the Weddell Front (WF). In the southern ACC this is the area between the WF and the Southern ACC Front

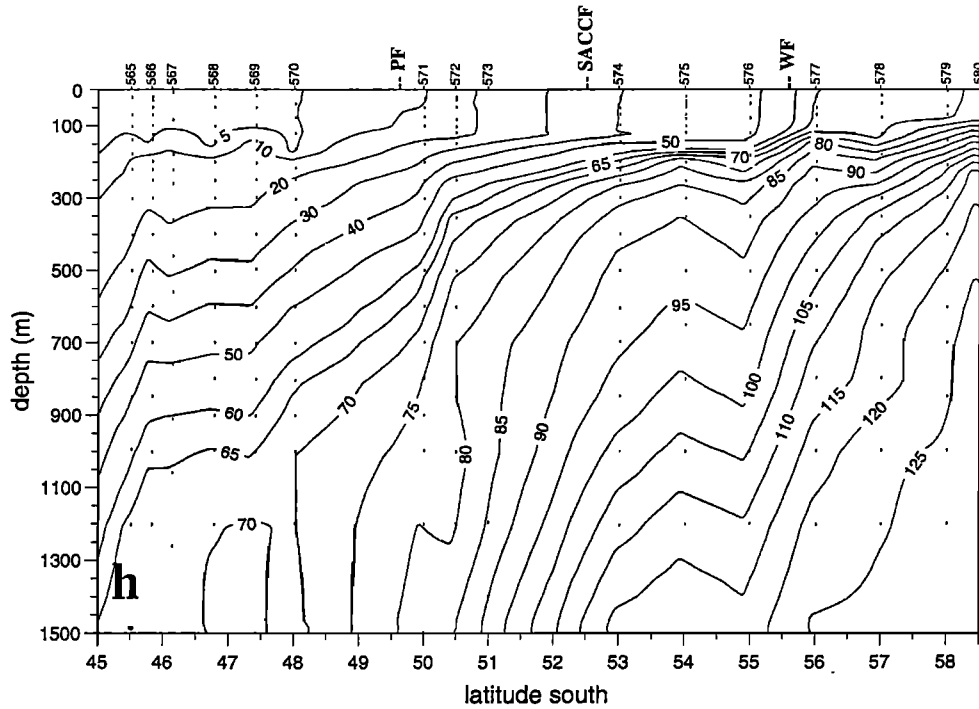


Figure 2. (continued)

(SACCF), which exhibits relatively homogeneous surface layer concentrations, whereas across the SACCF large horizontal gradients occur. Solving equations (1)–(3), we calculate  $F_{UCDW} = 0.90 \pm 0.34$  for the fraction of UCDW (with error propagation of all nitrate and phosphate concentrations). Thus the AASW of the southern ACC is produced from 90% UCDW and 10% of Weddell Sea surface water.

#### 4.2. Modification of Surface Layer Properties

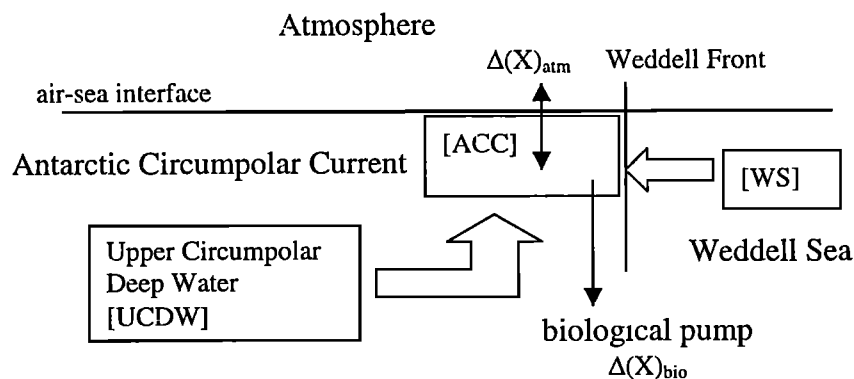
Since the fractions of source water masses of the AASW of the southern ACC are known, they can be used to estimate the conservative part of the concentrations of other properties. By difference with the actually measured concentrations then (Table 1), the nonconservative part is obtained. The nonconservative contribution of silicate,  $O_2$  and  $TCO_2$  is due to biological changes, whereas for the latter two gases,

exchange between ocean and atmosphere contributes additionally. When silicate concentrations from Table 1 and  $F_{UCDW} = 0.90 \pm 0.34$  are substituted into the silicate analogue of equation (1),  $\Delta(SiO_4)_{bio}$  of  $40 \pm 6 \mu\text{mol kg}^{-1}$  is obtained. Thus almost half of the original silicate content of the surface layer (compare Table 1) has been removed by diatoms.

Changes in  $TCO_2$  and  $O_2$  are estimated from equations (4) and (5):

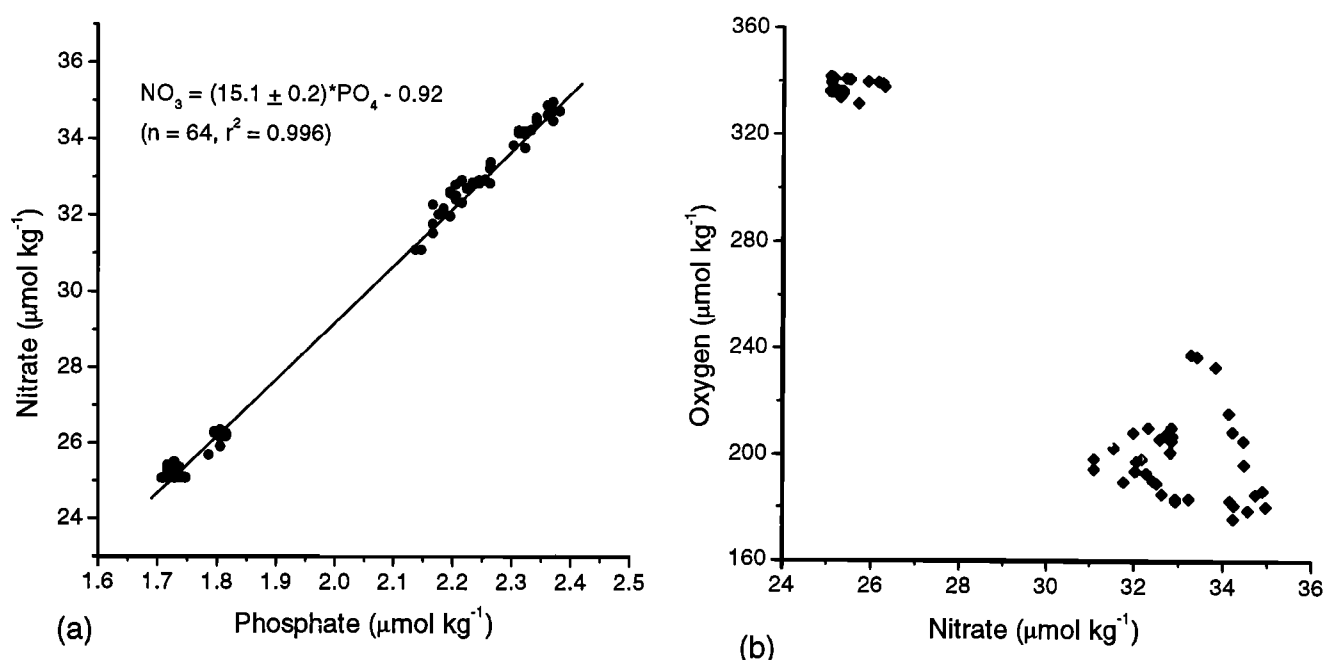
$$F_{UCDW} * [UCDW(TCO_2)] + (1 - F_{UCDW}) * [WS(TCO_2)] \\ = [ACC(TCO_2)] - \Delta(TCO_2)_{bio} - \Delta(TCO_2)_{atm} \quad (4)$$

$$F_{UCDW} * [UCDW(O_2)] + (1 - F_{UCDW}) * [WS(O_2)] \\ = [ACC(O_2)] - \Delta(O_2)_{bio} - \Delta(O_2)_{atm}, \quad (5)$$



**Figure 3.** Schematic representation of the water masses and processes along the prime meridian near the southernmost ACC. Boxes represent water masses; within brackets are the concentrations which refer to equations (1)–(7). The box containing [ACC] symbolizes the surface layer of the southernmost ACC. Open arrows show water mass flow. Solid arrows express processes that change the composition of the Antarctic Surface Water of the southern ACC. X is a particular property, such as nitrate or  $TCO_2$ .





**Figure 4.** Relationships between (a) the nitrate and the phosphate concentration and (b) the oxygen and the nitrate concentration for water < 2000 m in the southernmost area of the ACC. There is a gap in the data from the surface layer to the deeper layers. This is due to the extremely large gradients in the pycnocline, which is hard to capture in a regular sampling scheme.

where the terms denote the same as in equations (1) and (2), except for  $\text{TCO}_2$  and  $\text{O}_2$ .  $\Delta(\text{TCO}_2)_{\text{atm}}$  and  $\Delta(\text{O}_2)_{\text{atm}}$  are the changes resulting from exchange between ocean and atmosphere. Applying  $\text{FUCDW} = 0.90 \pm 0.34$  and the concentrations from Table 1 yields

$$\Delta(\text{TCO}_2)_{\text{bio}} + \Delta(\text{TCO}_2)_{\text{atm}} = -47 \pm 14 \quad (6)$$

$$\Delta(\text{O}_2)_{\text{bio}} + \Delta(\text{O}_2)_{\text{atm}} = +144 \pm 52. \quad (7)$$

Thus, through the combined action of biological processes and air-sea exchange the ACC surface layer lost  $47 \mu\text{mol kg}^{-1}$  and gained  $144 \mu\text{mol kg}^{-1}$  of  $\text{TCO}_2$  and  $\text{O}_2$ , respectively.  $\Delta(\text{TCO}_2)_{\text{bio}}$  and  $\Delta(\text{O}_2)_{\text{bio}}$  can be computed from  $\Delta(\text{NO}_3)_{\text{bio}}$

and  $\Delta(\text{PO}_4)_{\text{bio}}$  as obtained from equations (1)–(3), using the appropriate Redfield ratios of conversion. It is not feasible to derive C:N and C:P ratios from the in situ water masses (like for the N:P ratio, Figure 4a) because air-sea exchange of  $\text{CO}_2$  and  $\text{O}_2$  and mixing interfere with this method. This is illustrated in Figure 4b by a plot of  $\text{O}_2$  versus nitrate for this area, which is highly scattered. Table 2 presents different sets of Redfield ratios. Those of *Anderson and Sarmiento* [1994] are valid for all intermediate and deep ocean basins except the Southern Ocean and are currently considered the best available. In essence, they confirm the canonical *Redfield et al.* [1963] ratios. The ratios of *Hoppema and Goeyens* [1999] are valid for the surface waters of the nearby Weddell Sea.

**Table 1.** Data From Stations in the Southern ACC and Northern Weddell Sea Used for the Calculation of the Composition of the ACC Surface Water

Station	Total $\text{CO}_2$ , $\mu\text{mol kg}^{-1}$	$\text{NO}_3$ , $\mu\text{mol kg}^{-1}$	$\text{PO}_4$ , $\mu\text{mol kg}^{-1}$	$\text{SiO}_4$ , $\mu\text{mol kg}^{-1}$	$\text{O}_2$ , $\mu\text{mol kg}^{-1}$	Salinity	Potential Temperature $^{\circ}\text{C}$
<i>Southern ACC, Surface Water</i>							
574	2234.3	26.0	1.80	41.3	340.7	33.888	0.003
575	n.d.	26.0	1.77	44.3	336.2	33.912	-0.199
576	2237.4	27.0	1.87	47.0	339.2	33.900	-0.853
<i>Weddell Sea, Surface Water</i>							
577	2245.6	28.8	2.03	66.7	332.8	34.110	-1.005
578	2244.3	28.0	1.98	69.9	333.7	34.155	-1.213
<i>Upper Circumpolar Deep Water</i>							
574	2290.3	35.4	2.40	85.2	176.1	34.59	1.791
575	n.d.	35.3	2.39	85.9	179.3	34.58	1.602
576	2283.2	35.2	2.41	85.6	181.3	34.59	1.708

n.d. is not determined

**Table 2.** Redfield Ratios of Changes Due to Biological Activity for Carbon (C), Nitrogen (N), Phosphorus (P), and Oxygen (O<sub>2</sub>) From the Literature

	C:N	C:P	O <sub>2</sub> : N	O <sub>2</sub> :P
<i>Redfield et al.</i> [1963]	6.6	106		
<i>Anderson and Sarmiento</i> [1994]	7.3	117	-10.6	-170
<i>Hoppema and Goeyens</i> [1999]	5.7	93		
Average	6.5±0.8	105±12		

They are not significantly different from the canonical Redfield ratios. The *Redfield et al.* [1963] ratios involving O<sub>2</sub> are not shown in Table 2 because they are not derived from observations and are obviously erroneous. Using  $\Delta(\text{PO}_4)_{\text{bio}}$  and  $\Delta(\text{NO}_3)_{\text{bio}}$  from equations (1)–(3) amounting to  $-0.55 \pm 0.14 \mu\text{mol kg}^{-1}$  and  $-8.27 \pm 2.37 \mu\text{mol kg}^{-1}$ , respectively, we arrive at  $\Delta(\text{TCO}_2)_{\text{bio}}$  of  $-56 \pm 16 \mu\text{mol kg}^{-1}$  and  $\Delta(\text{O}_2)_{\text{bio}}$  of  $91 \pm 24 \mu\text{mol kg}^{-1}$ . Substituting this value of  $\Delta(\text{TCO}_2)_{\text{bio}}$  in equation (6) results in  $\Delta(\text{TCO}_2)_{\text{atm}}$  of  $+9 \pm 21 \mu\text{mol kg}^{-1}$  (surface layer has absorbed this amount of CO<sub>2</sub> from the atmosphere). Analogously, for  $\Delta(\text{O}_2)_{\text{bio}}$  and equation (7) this yields  $\Delta(\text{O}_2)_{\text{atm}}$  of  $+53 \pm 57 \mu\text{mol kg}^{-1}$ . This very large amount of oxygen is absorbed by the AASW of the southern ACC within the time frame typical for this surface layer (see below).

#### 4.3. Sensitivity of Calculations

Especially since surface waters are involved, the question as to the validity of the calculations is justified. The resulting value for FUCDW from equations (1) and (2) is crucial for all further calculations. Clearly, FUCDW is dependent on the concentrations of the end-members as well as on the ratio of biological changes of nitrate to phosphate (equation (3)). Possible errors due to dilution effects of the surface water by precipitation or melting of ice were removed by normalizing the concentrations to salinity 35. The nitrate to phosphate ratio in our study (15.1) is lower than the classical Redfield ratio of 16, but it is within the error range given by *Anderson and Sarmiento* [1994], and ocean wide values by *Fanning* [1992] and *Tyrrell and Law* [1997] are also closer to 15 than to 16. A similar lower nitrate to phosphate ratio of 15.2 was found in the surface water of the nearby western Weddell Sea [*Hoppema and Goeyens*, 1999]. Moreover, a ratio of 16 would yield an unrealistic result of FUCDW >1. Since the calculation is sensitive to the ratio, we used the ratio derived from our own field observations (Figure 2) to achieve better internal consistency.

Weddell Sea surface water flows into the southern ACC not only in winter but the whole year through. We used concentrations which derived from early winter in the AASW of the Weddell Sea. In summer, however, the concentrations of TCO<sub>2</sub> and nutrients in the surface layer of the Weddell Sea are significantly lower than in winter [*Hoppema et al.*, 1995; *Hoppema and Goeyens*, 1999], and thus the actual (mean) end-member concentrations are lower than those used in this study. Concentrations found in the Weddell Sea in summer give deviations from FUCDW generally less than 10%, indicating that the calculation is relatively insensitive to the Weddell Sea end-member. That summer concentrations of nitrate and phosphate would hardly change FUCDW is well

within expectation because in the Weddell Sea the ratio of change of nitrate to phosphate by biological activity is the same as in the southern ACC [see *Hoppema and Goeyens*, 1999].

The errors in  $\Delta(\text{TCO}_2)_{\text{atm}}$  and  $\Delta(\text{O}_2)_{\text{atm}}$ , computed with formal error propagation, are relatively large (end of section 4.2). FUCDW takes a central position in our analysis, and using this fraction allows us to deduce biological changes and air-sea exchange. The formal error in FUCDW is 37% (section 4.1). If FUCDW of 0.55 (lower boundary of error interval) is applied to equations (1)–(7),  $\Delta(\text{TCO}_2)_{\text{atm}}$  and  $\Delta(\text{O}_2)_{\text{atm}}$  of +6 and +28  $\mu\text{mol kg}^{-1}$ , respectively, are found. This shows that the derived atmospheric exchanges are little sensitive to errors in the end-members of mixing. Hence even using the lowest probable FUCDW generates values for  $\Delta(\text{TCO}_2)_{\text{atm}}$  and  $\Delta(\text{O}_2)_{\text{atm}}$  that are consistent with the above result that the southern ACC is a small sink for atmospheric CO<sub>2</sub> and a relatively large sink for atmospheric O<sub>2</sub>. This strongly hints that the actual errors in our estimates for  $\Delta(\text{TCO}_2)_{\text{atm}}$  and  $\Delta(\text{O}_2)_{\text{atm}}$  are much smaller than the formal errors. Below we give more indications for this contention.

## 5. Discussion

### 5.1. Timescale and Upwelling Velocity of UCDW

In the above balance calculations, changes in the Antarctic Surface Water of the southern ACC were identified which are caused by mixing as well as by biological and physical (air-sea exchange) processes. Assigning a time frame during which these processes take place would allow one to derive process rates, such as the upwelling velocity of UCDW. This is, however, somewhat problematic, but in the following it is shown that we can provide a fair estimate.

AASW of the southern ACC is formed all along the circumpolar track of the southern boundary of the ACC. Calculations in this paper indicate that the UCDW is the primary source water. UCDW originates from the deep waters of the Pacific and Indian Oceans. At the prime meridian its characteristics are acquired predominantly from the SE Pacific Ocean [*Callahan*, 1972; *Reid*, 1986] and transferred to the surface layer between the SE Pacific and the prime meridian. This implies that the deep water of the Pacific is to cross the ACC before it reaches the prime meridian. That this indeed occurs can be seen in *Whitworth and Nowlin* [1987] and *Orsi et al.* [1993], who evidence that the North Atlantic Deep Water, which is injected in the SW Atlantic (i.e., downstream of the SE Pacific), crosses the ACC before it reaches the prime meridian. Between the SE Pacific and the prime meridian a water parcel in the ACC travels some 5500 km. *Reid and Nowlin* [1971] and *Nowlin et al.* [1977] measured current speeds in the subsurface layers down to ~1000 m depth (which includes the core of the UCDW) of >10–20 cm s<sup>-1</sup>, while *Hofmann* [1985] reported speeds of 20–30 cm s<sup>-1</sup> for the nonfrontal area of the southern ACC as based on First GARP Global Experiment (FGGE) drifters (much higher speeds in the Polar Front). These data suggest that 20 cm s<sup>-1</sup> is an acceptable value for the mean speed of the surface and subsurface layers of the southernmost ACC, which is supported by acoustic doppler current profiler (ADCP) data on several crossings of the Drake Passage [*Wisotzki et al.*, 1995]. It will thus take the surface and subsurface layers ~1 year to travel the track of 5500 km between the SE Pacific and the prime meridian.

The winter surface mixed layer of the southern ACC on the prime meridian is ~110 m thick (Figure 2b). As 55-90% of this layer derives from the UCDW (sections 4.1 and 4.3) and the time frame is 1 year, the upwelling velocity in the southern ACC is as high as 60-100 m yr<sup>-1</sup>. This value compares very well with an estimate of up to 95 m yr<sup>-1</sup> for the ACC by *Gordon et al.* [1977]. Model analyses of the history of tritium in the surface layer in this region suggest comparably high upwelling velocities [*Butzin*, 1999]. *Comiso et al.* [1993] show a region of maximum upwelling in the ACC, which includes our study area. The actual values for the upwelling velocity shown by *Comiso et al.* [1993, Plate 4] are unrealistically high, as in our study area they would read 1000-1500 m yr<sup>-1</sup>. We assess the latter values are a factor 10 too high. Upwelling is known to be enhanced by circulation-topography interaction [*McCartney*, 1976]. In the southern ACC the southward flowing Circumpolar Deep Water meets the rising topography of the ridge system, consisting of the Scotia Ridge, North Weddell Ridge, and South Atlantic Ridge (see Figure 1), which apparently leads to a relatively high upwelling velocity.

The fact that our analysis comes to a result that compares well with other independent methods for determining the upwelling velocity puts much confidence in the method we used and the assumptions we made. This then not only holds for our calculated upwelling velocity but also for other results that derive from our analysis because upwelling and changes due to biological activity are closely intertwined and mutually dependent. It is evident that a large extent of upwelling, tending to raise the concentrations of the nutrients and TCO<sub>2</sub> in the surface layer, should be compensated by intense biological activity, oppositely drawing down these species.

## 5.2. Balance background

At this point, some remarks as to the background of the balance calculation and its results are in order. We calculated the fractions of the sources of the AASW of the southern ACC and derived a typical timescale of 1 year for the processes determining the composition of this AASW. The derived concentration changes of nutrients, TCO<sub>2</sub>, and oxygen due to the different causes (section 4.2) are the net changes on an annual basis. It is important to realize that reliable net changes can only be obtained when the processes considered are steady, i.e., not active. In particular, biological activity should be resting, i.e., at a minimum. If this were not the case the concentrations of the biologically mediated nutrients would for a smaller or larger portion be caused by seasonally varying primary productivity or remineralization. The calculated change due to biological activity would in that case be an unknown composite of the net annual change and the actual change due to active biology.

Our early austral winter data are perfectly suited in the light of such deliberations since the level of biological activity is close to its annual minimum [*Spiridonov et al.*, 1996]. Another asset of our analysis method is that knowledge of seasonal variations in the southern ACC is not required because the surface layer of the southern ACC acts as a memory for the net changes of the previous year. This holds both for the surface layer concentrations as well as for the mixed layer depth. An exception is the seasonal behavior of the nutrient concentrations of the inflowing AASW from the Weddell Sea: Such inflow occurs throughout the year, but in summer the nutrient concentrations are lower than in winter.

In section 4.3 the effect of using summerlike nutrient concentrations on the budget calculation was found to be small.

## 5.3. CO<sub>2</sub> and Oxygen Sinks

This study found the southernmost ACC to be a small sink for atmospheric CO<sub>2</sub> and a very large sink for atmospheric oxygen on an annual basis. Here these results are discussed in terms of physical and biological processes. In addition, we substantiate our results by comparing them with studies using different methods.

Upwelling of UCDW tends to increase the CO<sub>2</sub> content of the surface layer and thus also the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>), which may lead to supersaturation with respect to the atmospheric pCO<sub>2</sub>. We estimate the pCO<sub>2</sub> for UCDW to be ~500 µatm, using TCO<sub>2</sub> of 2260 µmol kg<sup>-1</sup> (Table 1) and alkalinity derived from the relationship  $\text{alk} \cdot (35/\text{salinity}) = 2386 \text{ } \mu\text{mol kg}^{-1}$ , as given by *Poisson and Chen* [1987] for this region. This would lead to outgassing of CO<sub>2</sub> to the atmosphere. However, as we found the southern ACC to be a sink for atmospheric CO<sub>2</sub>, an annual mean undersaturation must be prevalent in the surface layer. Two mechanisms promote the reversal of the trend toward supersaturation in the surface layer. First, upon upwelling the temperature and salinity decrease by >3°C and ~0.7 salinity units, respectively. On the basis of these changes only we calculate the reduction of pCO<sub>2</sub> to be 70-90 µatm. Second, the decrease of TCO<sub>2</sub> due to biological activity, amounting to 56 µmol kg<sup>-1</sup> (section 4.2), would reduce the pCO<sub>2</sub> of the upwelled UCDW by ~165 µatm, which in itself is enough to cause undersaturation. This suggests that for establishing the CO<sub>2</sub> sink in the southern ACC, biological drawdown of CO<sub>2</sub> is more important than physical processes.

Can we find any indications from other studies that may corroborate our results? From pCO<sub>2</sub> measurements a qualitative picture may be obtained, which could illustrate the relative importance of certain processes in different seasons. Unfortunately, the temporal and spatial coverage of pCO<sub>2</sub> data in this region is so scarce that calculated annual air-sea fluxes are not reliable. In early austral spring, pCO<sub>2</sub> in the southern ACC at 6°W was close to full or slightly below saturation [*Bakker et al.*, 1997]. This reflects the onset of photosynthesis. In summer a substantial undersaturation of CO<sub>2</sub> is found for the southern ACC in most of the Atlantic sector of the Southern Ocean [*Takahashi et al.*, 1993]. This is obviously the time of year that CO<sub>2</sub> is being incorporated into organic matter. In austral autumn a small supersaturation of CO<sub>2</sub> was observed in our area of investigation [*Hoppema et al.*, 2000], which can be explained by a temporal preponderance of upwelling of TCO<sub>2</sub>-rich UCDW, possibly accompanied by some remineralization activity. Winter data from the South Atlantic [*Takahashi et al.*, 1993] reveal both supersaturation and undersaturation of CO<sub>2</sub>. In summary, pCO<sub>2</sub> data suggest that CO<sub>2</sub> uptake from the atmosphere probably occurs mainly in summer. This region has the potential to take up substantial amounts of CO<sub>2</sub> in summer because even in summer the wind speeds are relatively high, wind action promoting the CO<sub>2</sub> exchange between the air-sea interface.

As regards O<sub>2</sub>, a similar calculation can be performed. UCDW has a low O<sub>2</sub> concentration (Table 1), the percentage of saturation being only 53-54%. Consequently, upwelling produces a marked undersaturation of oxygen in the surface

layer. This undersaturation is even reinforced by cooling and freshening of the upwelled UCDW, which would bring down the saturation level to ~48%. These processes are counteracted by biological activity, which increases the  $O_2$  concentration by  $91 \mu\text{mol kg}^{-1}$  (section 4.2). This  $O_2$  increase would bring the upwelled UCDW to ~80% saturation (without cooling/ freshening) or 75% (including cooling/freshening). Apparently, the  $O_2$ -reducing effects of upwelling and cooling/ freshening far outdo the  $O_2$ -increasing effect of primary production in the southern ACC. The large  $O_2$  undersaturation of the UCDW is the most important factor for the large  $O_2$  sink of the southern ACC.

The  $O_2$  uptake in the southern ACC calculated in this study is much larger than that in the Weddell Sea [Hoppema *et al.*, 1995]. The main reason is the much larger transfer of  $O_2$ -poor water into the surface layer in the southern ACC than in the Weddell Sea owing to the much higher upwelling velocity in the southern ACC. North of our area of investigation (in particular, north of the Polar Front), upwelling of deep waters into the local surface waters does not occur. As the upwelling of  $O_2$ -poor deep water is a major trigger for the uptake of large amounts of atmospheric  $O_2$  by the ocean, we surmise that the ocean in this northern region is a source of  $O_2$  due to biological activity. The composite picture emerges of a regional distribution of air-sea exchange of  $O_2$  with a precipitous peak of  $O_2$  uptake by the southern ACC in between two areas where the  $O_2$  uptake is moderate or absent. This picture is perfectly in line with the regional distribution of the atmospheric  $O_2$  concentration between the South Pole and Tasmania [Stephens *et al.*, 1998]. In the atmospheric  $O_2$  distribution, there is a major latitudinal anomaly of low  $O_2$  concentration over the Southern Ocean. In fact, Stephens *et al.* [1998] invoked latitudinal variation in the air-sea exchange of  $O_2$  to bring their modeled atmospheric  $O_2$  in agreement with the measurements. Our analysis suggests that the low atmospheric  $O_2$  concentration over the Southern Ocean is caused by the immense uptake of  $O_2$  by the ocean in the southern ACC region. Distributed over a mixed surface layer of ~110 m,  $\Delta(O_2)_{\text{atm}}$  of  $53 \mu\text{mol kg}^{-1}$  can be converted into a total  $O_2$  uptake by the southern ACC of  $\sim 6.0 \text{ mol m}^{-2} \text{ yr}^{-1}$ . Compared to the results of three different ocean models as given by Stephens *et al.* [1998], our calculated  $O_2$  uptake, which we consider very high, is on the lower side. We assess the  $O_2$  sink of the Southern Ocean is overestimated by these models. A smaller Southern Ocean sink would indeed improve the agreement of those models with the atmospheric  $O_2$  measurements [Stephens *et al.*, 1998].

#### 5.4. Estimates of Productivity

Applying the typical timescale of 1 year in which processes in the southern ACC surface layer take place, the absolute changes of  $\text{TCO}_2$  and nutrients due to biological activity can be converted to annual utilization rates. For  $\text{TCO}_2$  the absolute change of  $56 \pm 16 \mu\text{mol kg}^{-1}$  (section 4.2), distributed over a mixed layer of 110 m, yields a carbon utilization of  $6.3 \pm 1.8 \text{ mol C m}^{-2} \text{ yr}^{-1}$  or  $76 \pm 22 \text{ g C m}^{-2} \text{ yr}^{-1}$ . Our method to obtain  $\Delta(\text{TCO}_2)_{\text{bio}}$  and the annual carbon utilization in principle renders the net change of carbon in the surface layer. Hence the calculated annual utilization would equal the new production or export production. However, in our case the residence time of the water in the surface layer of 1 year is typically the same timescale on which the biological

cycle in the surface layer takes place. This leads to interference between these two causes of nutrient changes in the surface layer, with the consequence that the our annual carbon utilization does no longer represent the pure new production. Instead, it represents a lower boundary for the total annual primary production.

Our annual carbon utilization, which represents an open ocean value, is much higher than traditional, incubation-based estimates of the primary production in open ocean Antarctic waters, which are  $<20 \text{ g C m}^{-2} \text{ yr}^{-1}$  [e.g., Jacques, 1989]. However, also previously elevated primary production was reported for the southern ACC [Dafner and Mordasova, 1994; Tynan, 1998]. In addition, on the basis of a bio-optical algorithm using satellite (Coastal Zone Color Scanner) observations, a Southern Ocean mean primary production of  $>100 \text{ g C m}^{-2} \text{ yr}^{-1}$  was reported [Arrigo *et al.*, 1998]. The latter value compares fairly well with our estimate, and thus our study supports the notion of a moderately high mean primary production of the Southern Ocean, rather than an oligotrophic region with very low productivity. Further supporting this view is a modeling study indicating the Antarctic Ocean as a significant sink of atmospheric  $\text{CO}_2$  mainly due to the action of the biological pump [Louanchi *et al.*, 1999].

Given the current debate around the mean level of primary production in the Southern Ocean, it is difficult to decide whether the southern ACC represents an area of elevated productivity or just an average region within the Southern Ocean. We may, though, try to explain the primary production in the southern ACC in the light of prevalent biotic and abiotic conditions. Biological studies suggest that the southern ACC is a region with low productivity, characterized by the absence of phytoplankton blooms [Bathmann *et al.*, 1997]. However, blooms have been reported in the region, even in winter [Dieckmann, 1987], and according to Tynan [1998], the southern ACC is characterized by high productivity. Also during our early winter cruise ANT X/4, horizontal chlorophyll *a* and biogenic silica maxima were observed in the southernmost ACC near the Weddell Front [Spiridonov *et al.*, 1996]. Physical conditions do not seem to be optimal in the southern ACC, where frequent storm events result in a deep mixed layer, which in turn could suppress the development of phytoplankton blooms. Notwithstanding this widely accepted view, bloom development has been observed near the Polar Front where the mixed layer depth was as deep as  $>70 \text{ m}$  [De Baar *et al.*, 1995]. Thus despite the adverse physical conditions in the southern ACC a high level of primary production is feasible. De Baar *et al.* [1995] have demonstrated that shortage of iron is at least one of the factors influencing phytoplankton growth in this part of the Southern Ocean. As noticeable in the work of De Baar *et al.* [1995], UCDW has a relatively high concentration of iron compared to the surface water of the southern ACC. This implies that upwelling of UCDW tends to increase the iron concentration of the surface layer and hence stimulate phytoplankton growth. As the upwelling velocity in the southern ACC is high, the supply of iron is probably relatively large. Of course, the level of primary production also depends on other factors, but the ample availability of iron is definitely a prerequisite.

In a similar way as above for carbon, using  $\Delta\text{Si}_{\text{bio}} = 40 \pm 6 \mu\text{mol kg}^{-1}$  (section 4.2) and a mixed layer depth of 110 m, the annual silicate consumption is calculated to be  $4.5 \pm 0.7 \text{ mol}$

$\text{Si m}^{-2} \text{ yr}^{-1}$  or  $126 \pm 19 \text{ g Si m}^{-2} \text{ yr}^{-1}$ . Similar to the carbon utilization, this silicate consumption is substantially higher than previous estimates of  $\sim 40 \text{ g Si m}^{-2} \text{ yr}^{-1}$  (converted from the total Antarctic silica production of  $47 \text{ Tmol yr}^{-1}$  [Tréguer and Van Bennekom, 1991]). On the basis of a comparison of surface transects, Van Bennekom et al. [1988] calculated silicate consumption rates amounting to  $56 \text{ g Si m}^{-2} \text{ yr}^{-1}$  in an area south of the Polar Front at  $10^\circ\text{E}$ . Part of the discrepancy between the latter value and ours may arise because of the significant wintertime phytoplankton production, as evidenced by relatively high biogenic silica values [Spiridonov et al., 1996], which is not included in the estimate of Van Bennekom et al. [1988].

The silicate to carbon utilization as derived in the present study amounts to  $\text{Si:C} = 0.71 \text{ mol mol}^{-1}$ , and accounting for the fact that diatoms constitute only 75% of the total phytoplankton production [Tréguer et al., 1995], this is reduced to  $\text{Si:C} = 0.53 \text{ mol mol}^{-1}$ . This is much higher than the  $0.13 \text{ mol mol}^{-1}$  found for diatoms in nutrient-replete conditions [Brzezinski, 1985]. However, our elevated ratio is in keeping with evidence that diatoms produce 2–4 times as much silica per unit carbon in the Southern Ocean as in other ocean regions [Nelson et al., 1989; Leynart et al., 1991], which is due to iron limitation [Takeda, 1998]. This consistency further increases the reliability of our results.

Previous investigations on silicate have shown that the southernmost region of the ACC is an outstanding region [Van Bennekom et al., 1988]. The sediments in this region are rich in biogenic opal [DeMaster, 1981], in contrast with areas farther south such as the Weddell Sea. A high production of biogenic silica (opal) by diatoms in the surface layer in general terms favors the transfer of opal tests to the seafloor. Thus the high silica production in this area could be a crucial factor for the occurrence of extensive silica-rich sediments.

## 6. Conclusions

We applied a new approach using nitrate and phosphate and their Redfield ratio to derive the composition of the Antarctic Surface Water of the southern ACC. For calculations involving surface waters these nutrients are very useful indeed because they have a negligible atmospheric component and a stable Redfield ratio. It is essential, though, that winter concentrations are used to exclude spatio-temporal effects. This may be a disadvantage since winter data are generally hard to obtain.

The UCDW fraction of 90% for the AASW of the southern ACC points to a large upwelling velocity. Since intensive upwelling transports large amounts of nutrients and  $\text{CO}_2$  into the surface layer, the biological utilization of these elements is accordingly high. The contribution of northward flowing AASW from the Weddell Gyre is relatively small with 10%. This suggests that exchange of surface water across the southern boundary of the ACC is restricted.

We found a large oxygen sink for the southern ACC, but the formal error in this estimate is large. There are strong indications (section 5.3) that this sink is real, and thus the actual error is smaller. The significant oxygen sink conforms with the latitudinal distribution of atmospheric oxygen. Also, the mean saturation level of the surface water after accounting for upwelling and cooling/freshening is definitely below 100%. The major cause of the oxygen sink is upwelling of

strongly undersaturated UCDW. A small  $\text{CO}_2$  sink with a large error was derived for the southern ACC. Also in this case the real error is much smaller, and we assess that the southern ACC is neutral or a slight  $\text{CO}_2$  sink. UCDW upwelling tends to raise  $\text{CO}_2$  in the surface layer, and this is mainly counteracted by biological activity.

Annual biological utilizations of carbon and silicate as derived here are significantly higher than most Southern Ocean estimates in the literature. Our carbon utilization supports recent elevated mean primary production estimates for the Southern Ocean. Our silicate to carbon utilization ratio agrees well with data from phytoplankton investigations showing much higher values in the Southern Ocean than in other oceanic regions. It would suggest that the silica production in the Southern Ocean is substantially underestimated by Tréguer et al. [1995]. In fact, raising the Southern Ocean primary production would indeed also increase the latter estimation of silica production.

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H.J.W. de Baar, Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB Texel, The Netherlands. (debaar@nioz.nl)

E. Fahrbach, Alfred-Wegener-Institut für Polar- und Meeresforschung, Bussestrasse 24, D-27570 Bremerhaven, Germany. (efahrbach@awi-bremerhaven.de)

M. Hoppema, University of Bremen, FB1, IUP, Department of Tracer Oceanography, P.O. Box 330440, D-28334 Bremen, Germany. (hoppema@physik.uni-bremen.de)

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